

REVINSON, DAVID

APPROVED
(FINAL FORM)

(SIGS OK)

~~(PROF. HOLMES HAS
ONE COPY)~~



AM
1944
re





BOSTON UNIVERSITY
GRADUATE SCHOOL

Thesis

A COMPARISON OF THE MICRO AND THE MACRO METHODS
FOR THE
DETERMINATION OF THE PHASE DIAGRAM OF THE SYSTEM,
SODIUM NITRATE-AMMONIUM NITRATE

By

David Revinson

(B.S., Canisius College, 1941)
submitted in partial fulfilment of the
requirements for the degree of
Master of Arts

1941~~7~~

an
L.C.

Am
1944
re

ACKNOWLEDGEMENT

In sincere appreciation I wish to acknowledge
the interest and helpful guidance of
Dr. E.O. Holmes, Jr.; without which
this work could not have been accomplished.



Digitized by the Internet Archive
in 2013

<http://archive.org/details/comparisonofmicr00revi>

APPROVED

by

First Reader.....*Edward C. Holmes Jr.*.....
Professor of Chemistry

Second Reader.....*J. Philip Mason*.....
Professor of Chemistry

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION.....	1
MATERIALS AND METHODS.....	2
Purification of materials.....	2
Drying of materials.....	3
Description of the apparatus used in micro method.	3
Description of the micro method.....	7
Description of the macro method.....	9
EXPERIMENTAL.....	11
Data found by other investigators.....	11
Data from materials dried over calcium chloride...	13
Data from materials dried over Anhydrone.....	15
Data from material purified by precipitation.....	15
DISCUSSION OF RESULTS.....	16
Significance of the data.....	16
Representative phase diagram for the system, ammonium nitrate-sodium nitrate.....	18
SUMMARY.....	19
FOOTNOTES.....	20

INTRODUCTION

The National Research Council undertook to uncover as much information as possible about the eutectics formed in the binary system A-B, where A is ammonium nitrate. Many universities accepted research work from the council along these lines. Before they started, it was recommended that they calibrate their technique with the data of the ammonium nitrate-sodium nitrate system as furnished by Early and Lowry.^(1,2) Instead of employing the cooling curve method and using large quantities of material, it was recommended for them to use the capillary tube technique since it was claimed that results could be duplicated satisfactorily.

Boston University was given some work to do and accordingly Professors E.O. Holmes, Jr. and J.P. Mason⁽³⁾ first undertook to calibrate their technique from the data of Early and Lowry.^(1,2) Each, working independently of each other, obtained values which checked very closely. However, these values in many cases were from one to five degrees different from those of Early and Lowry.^(1,2) Accordingly, this work was undertaken with the idea to find, if possible, the reasons for these discrepancies.

A review of the existing literature was able to give no further information on this system that was not already furnished by Early and Lowry.^(1,2)

MATERIALS AND METHODS

The ammonium nitrate used was furnished by the National Research Council and was of the highest grade purity obtainable. Further purification by recrystallization was not resorted to because of the fact that ammonium nitrate is explosive. The material was prepared for use by grinding it with an agate mortar and pestle and then spread in a thin layer on a watch glass. Then the whole was placed in a desiccator with a solid drying agent. Throughout all the experiments, the moisture content of the ammonium nitrate was kept constant and at a negligible value by the use of Anhydrone, a magnesium perchlorate dryer.

The sodium nitrate used was furnished by Merck and Company and was of reagent quality. Nevertheless, one portion was purified by three recrystallizations, while a second portion was purified by the common ion effect, that is, a concentrated nitric acid solution was added to the mother liquor so as to precipitate the sodium nitrate. In order to remove the odor of the acid, the crystals were first washed with distilled water and then recrystallized twice. This was done to see if there was any effect on the system due to a difference of the mode of purifying A. Since B, or ammonium nitrate, was used as furnished and kept very dry, a comparison could thus be of some value.

Not only was an attempt made to see if the mode of purification effected the results, but also an attempt was made to see if the moisture content of A caused the discrepancies

between the work of Early and Lowry^(1,2) and that of Holmes and Mason.⁽³⁾ This was done because of the fact that a few determinations made with the latter's materials, which stood approximately a half year over Anhydrone, seemed to indicate that still different values could be obtained.

Two different moisture contents were used. One consisted of placing the pulverized sodium nitrate on watch glasses and allowing them to remain in desiccators of anhydrous calcium chloride for about two weeks after recrystallization. The other was to place the pulverized sodium nitrate on watch glasses and to allow them to remain in desiccators of Anhydrone for about a month. Since the salt has a tendency to retain any moisture "even when attempts are made to remove it drastically⁽¹⁾," it was periodically removed and ground so more fresh surface area could be exposed to the drying agent.

In the determination of the eutectics by the capillary tube or micro method, a few modifications were applied to the suggestions offered by the National Research Council. Since Holmes and Mason⁽³⁾ could not get independent checks using the Thiele-Dennis melting point bath, it was discarded and in its place was used the usual melting point apparatus. However, a few modifications were made in this set up, especially in the manner as to how the heat was applied and as to how the capillary tubes were held in the oil bath. These modifications can be easily seen in Figures 1-3.

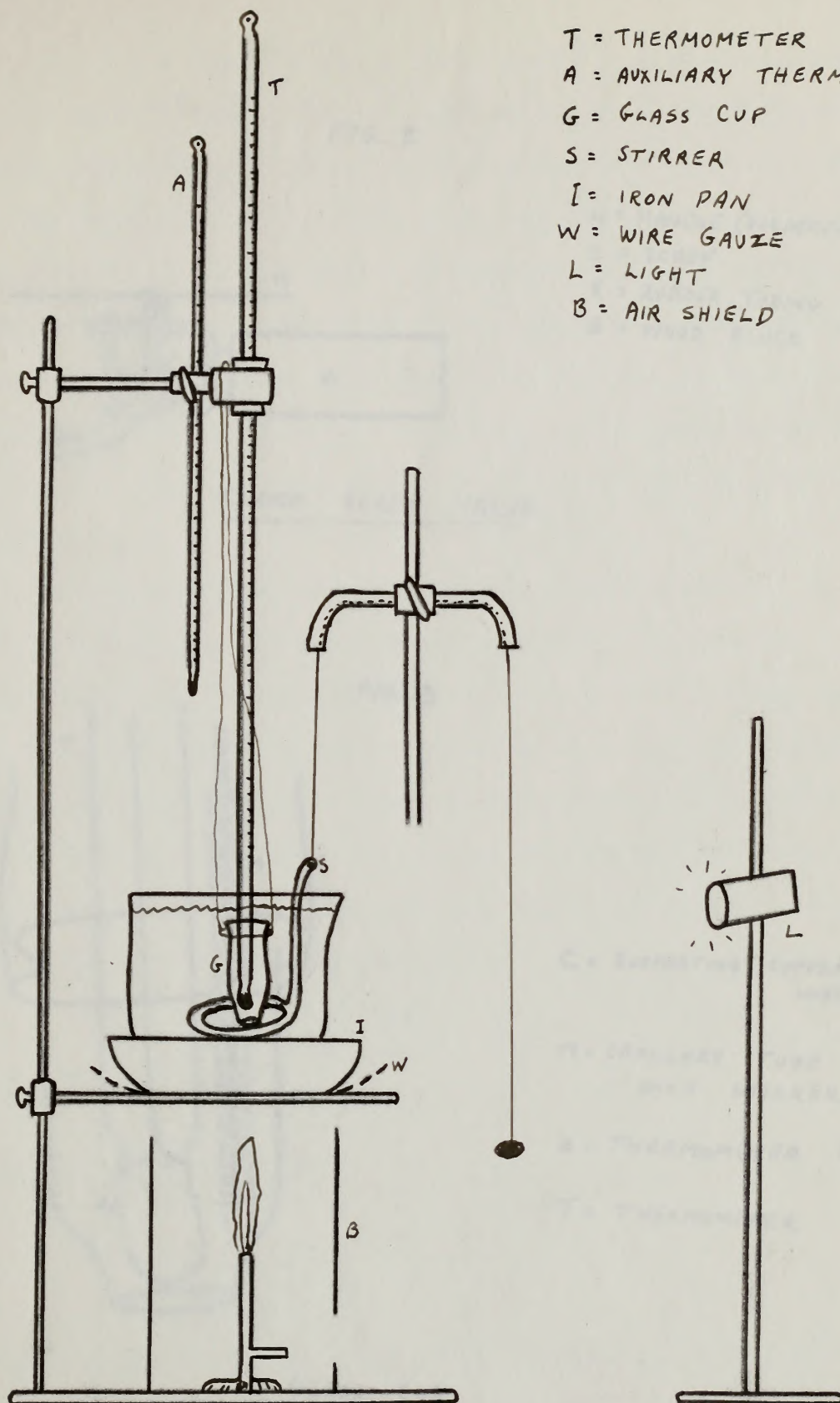
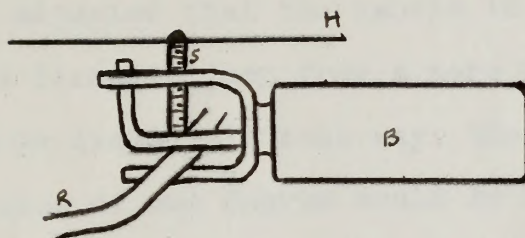


FIG. 1

FIG. 2



H = HANDLE (SOLDERED)

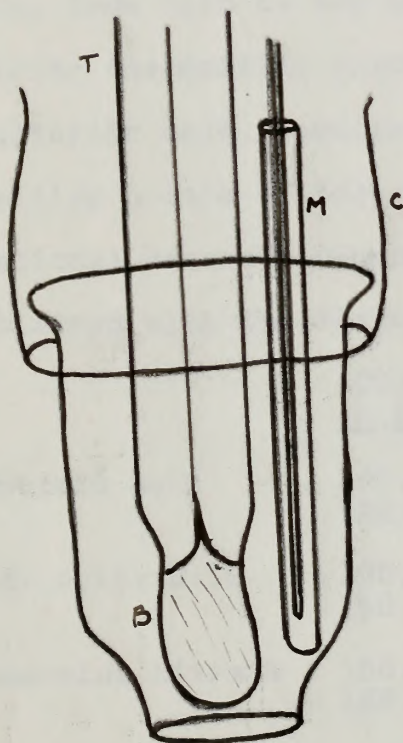
S = SCREW

R = RUBBER TUBING

B = WOOD BLOCK

CLAMP SCREW VALVE

FIG. 3

C = SUPPORTING COPPER
WIREM = CAPILLARY TUBE
WITH STIRRER

B = THERMOMETER BULB

T = THERMOMETER

GLASS CUP

To apply heat to the system, a micro burner was used and the amount of gas it burned was regulated by a unique clamp screw valve set up. This is well shown in Figure 2. The noteworthy fact about this regulation was that the clamp screw was so adjusted that the handle in swinging through 180° , caused the flame to jump from a mere pin point to a comparatively large flame. In this way, the bath could be so heated that a rise of one degree could be gotten every three minutes and thus give a greater degree of accuracy in obtaining the eutectic points.

The thermometer used was one that was graduated into tenths of a degree from 99°C. to 200°C. It was two feet long from bulb to top and was calibrated before usage by determining the melting points of several pure compounds such as salicylic acid, benzoic acid and ammonium nitrate. The exact melting points of these compounds were furnished by the National Research Council and the following was the data obtained with the thermometer:

	Obs. M.P.	Aux. Temp.	Corr. M.P.	Furnished M.P. of N.R.C.	Correction
Benzoic Acid	122.3 122.1	55 40.8	122.5 122.5	122.5	0
Salicylic Acid	158.8 158.9	41 51	160.0 160.0	159.8	-0.2
Ammonium Nitrate	168.7 168.8	51 57	170.1 170.1	169.6	-0.5

From a graph of these values, the correction factor for any temperature observed could be easily read off. The following equation was used to give the corrected melting point t_c :

$$t_c = t_o + (L)(0.000154)(t_o - t_m)$$

where t_o is the observed reading, L is the length in degrees of the exposed mercury thread above the level of the bath, and t_m is the average temperature of the exposed mercury thread. This latter was determined by placing a small auxiliary thermometer in such a manner so that its bulb was adjacent to the stem of the large thermometer and at a point about halfway between the surface of the bath and the top of the mercury thread. The bath used consisted of a colorless high boiling oil called Blandol and was furnished by the Howe and French Company.

Capillary melting point tubes used in calibrating the thermometer were of one millimeter bore. For the eutectic mixtures, tubes up to two millimeters bore were used, as they made observations of the sample easier, and efficient stirring could be accomplished. Thin glass rods of smaller diameter than the tubes were used as stirrers and were inserted within the tubes to keep the mixture agitated. If this were not done, it was found that the results obtained were never reliable. A glass cup as diagrammed in Figure 3 was hung below the mercury bulb of the thermometer so as to hold the capillary tubes in place even when stirring the mixture. Of great aid was a small light bulb so placed that it threw a path of light through the oil bath and also through the eutectic mixture. This enabled one to see very clearly any crystal formation or disappearance.

The procedure used in the micro determinations was the

one recommended by the National Research Council. Each sample for each freezing point determination consisted of about 0.10 gram total weight. The ammonium nitrate and the sodium nitrate were each weighed on a piece of black glazed paper and then carefully brushed off by a camel hair brush into a small test tube. While transferring the salt, another piece of black glazed paper was placed under the tube to catch any grains that happened to miss the mark. Then the mixed sample was melted over an oil bath to insure complete uniformity. After cooling, the melt was loosened from the tube, placed in an agate mortar, and then pulverized. This powder was then transferred to the capillary tube of two millimeters bore by conventional methods and the length of mixture column was made about 8 - 12 mm. long. The loaded tube was finally placed in the glass cup in the oil bath and next to the thermometer bulb.

In determining values, heat was applied rapidly until the temperature was about five degrees below the freezing point. Then it was applied very slowly so that the temperature rose only about one degree every two or three minutes. Meanwhile, the oil bath was agitated to insure a uniform temperature. The sample at first softened and gradually became liquid. At the point where the last crystal could be seen to disappear with constant stirring by means of the small stirrer, the temperature was noted. This was the eutectic point of the sample and could be rechecked by resolidifying and remelting the material in the tube. A series of such determinations

were made so that a phase diagram for that particular system could be plotted.

The procedure used in the macro determinations was a modification of the method used by Early and Lowry.^(1,2) Their apparatus consisted of an inner tube containing the salt mixture and this in turn was surrounded by an air-jacket which was supposed to prevent over-rapid cooling. The ammonium nitrate was weighed into the inner tube and was then followed by the sodium nitrate. About twenty grams was the combined weight of the two salts in each determination. Then the mixture was completely melted and a thermometer was clamped so that it was within the inner tube and extended into the liquid. By constant stirring of the mixture and by the radiation of heat from the inner tube, the temperature was allowed to drop. The point at which the formation of crystals first took place was plotted in the phase diagram.

However, when this procedure was followed, such a quick drop in temperature occurred that it seemed that one was lucky to obtain values which could be correct to one degree. Thus, instead of using an air bath, the oil bath as used in the micro determination was taken advantage of. The salt was weighed into a large test tube and this in turn was placed in the oil bath. After melting the mixture, the thermometer was clamped so that it extended into the test tube and entered the melt. This gave a much more satisfactory control of heat since the temperature could be lowered one degree every three minutes.

Throughout all the experiments, care was taken in handling the ammonium nitrate because of its explosive nature. In carrying out the operations of grinding and heating, the work was done behind a safety shield clamped to the laboratory table. During the course of the work, no accidents occurred.

EXPERIMENTAL

Using the macro apparatus, as described previously, Early and Lowry^(1,2) obtained the following values for the ammonium nitrate-sodium nitrate system:

<u>Table 1</u>	
<u>% NaNO₃</u>	<u>Temperature</u>
0	169.6
5	156.5
10	144.2
15	132.0
17.5	126.3
18.5	124.3
20.0	121.9
22.0	124.8
23.0	126.6
23.5	129.1
25.0	133.4
30.0	147.0
40.0	174.2

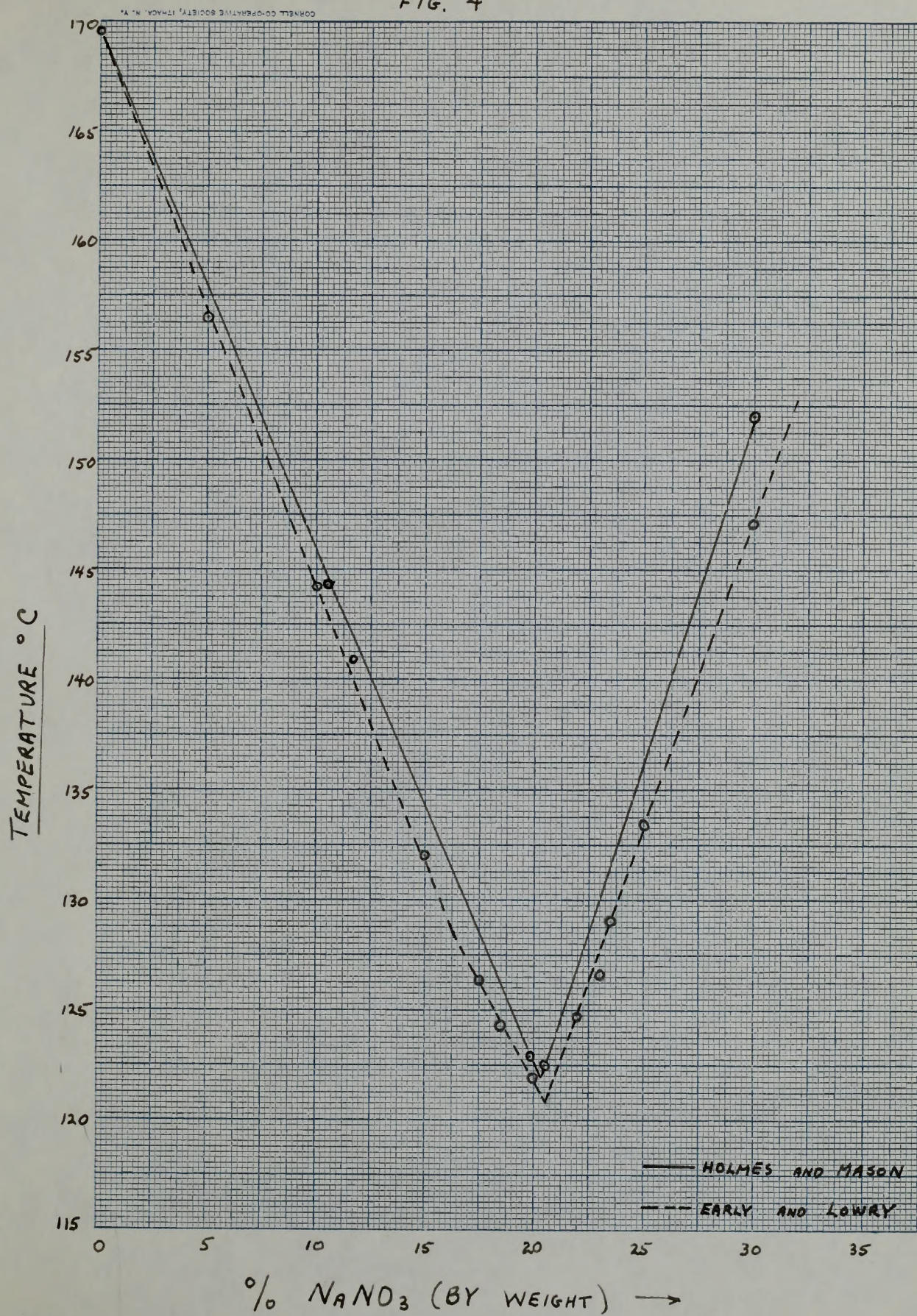
Holmes and Mason⁽³⁾ obtained the following values using the micro method:

<u>Table 2</u>	
<u>% NaNO₃</u>	<u>Temperature</u>
10.5	144.3
11.6	140.8
19.8	122.9
20.5	122.5
30.0	152.0

The difference in these two sets of values is clearly shown in Figure 4. This difference is what caused the undertaking of the present work.

After a few preliminary determinations which further indicated that the values of Early and Lowry^(1,2) were low, fresh sodium nitrate was procured and purified as previously explained. After standing over anhydrous calcium chloride for two weeks, the results obtained using recrystallized

FIG. 4



sodium nitrate in both the macro and micro methods, can be seen from Tables 3 and 4.

Table 3 - Macro Method

<u>% NaNO₃</u>	<u>Obs. Temp.</u>	<u>Aux. Temp.</u>	<u>L</u>	<u>Therm. Corr.</u>	<u>Corr. Temp.</u>	<u>Av. Temp.</u>
10.00	144.8	35	60	-0.1	145.7	145.8
	144.8	42	60	-0.1	145.8	
18.00	126.2	50	41	0	126.7	126.7
19.00	123.8	37	39	0	124.3	124.4
	123.9	31	39	0	124.5	
21.50	122.8	51	38	0	123.2	123.2
	122.8	45	38	0	123.3	
28.00	144.5	41	60	-0.1	145.4	145.3
	144.4	35	59	-0.1	145.3	

Table 4 - Micro Method

11.30	141.3	46	52	-0.1	142.0	142.0
	141.2	44	52	-0.1	141.9	
19.60	123.1	58	34	0	123.4	123.3
	123.0	64	34	0	123.3	
22.45	126.4	73	37	0	126.7	126.6
	126.3	69	37	0	126.6	
28.77	148.3	58	59	-0.1	149.0	149.0

Figure 5 shows how these values compare with each other, and with the work of Holmes and Mason.⁽³⁾ It can be seen that the macro and micro determinations are consistent and approximate the work of Holmes and Mason⁽³⁾ quite closely.

Following this, determinations were made on material which stood for one month over Anhydrone. Tables 5 and 6 give the results obtained with sodium nitrate purified by recrystallization, while Tables 7 and 8 give the results obtained by using sodium nitrate purified by precipitation. Figure 6 is the graphical representation of Tables 5-8.

FIG. 5

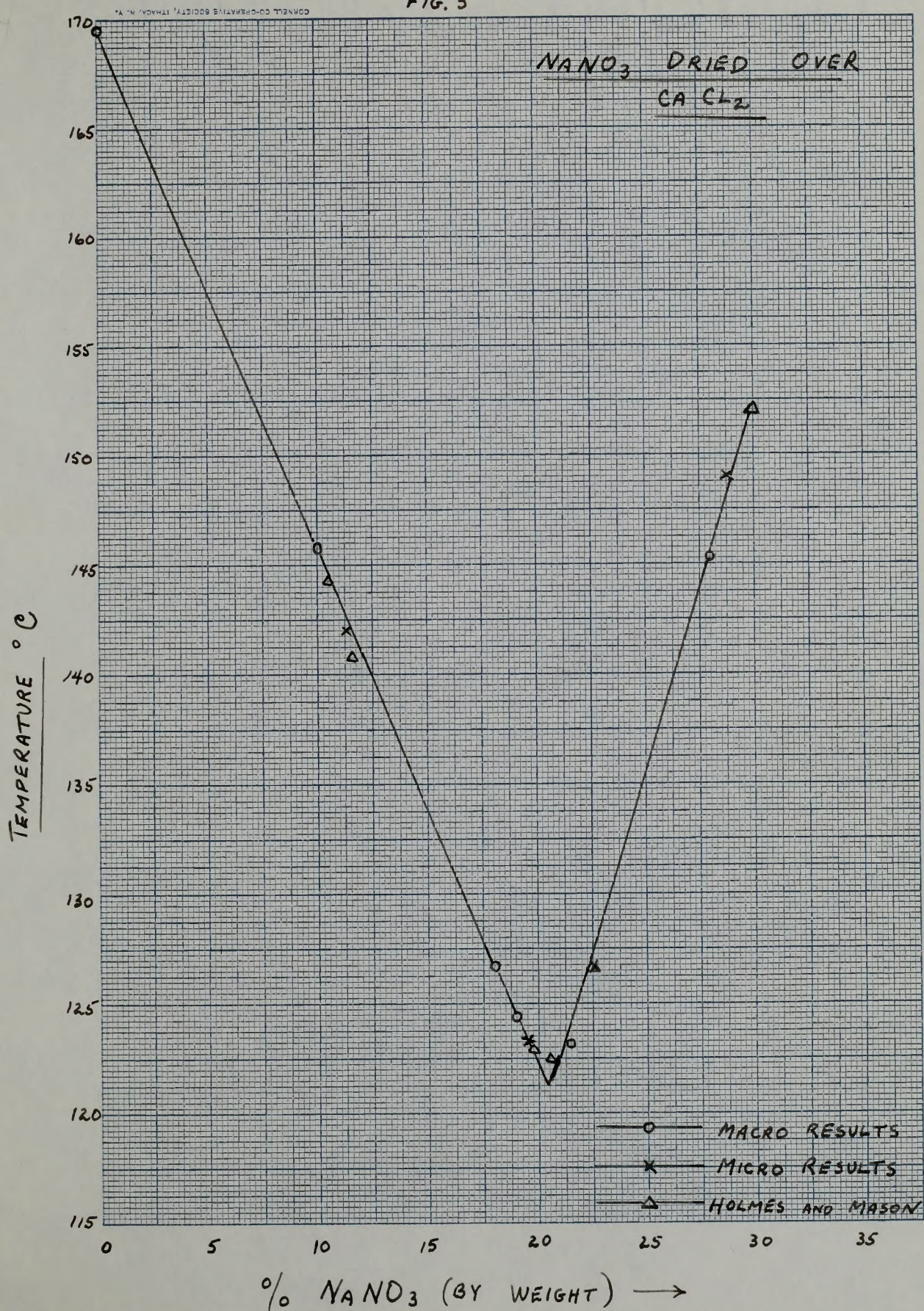


Table 5 - Macro Method on Recrystallized NaNO_3

<u>% NaNO_3</u>	<u>Obs. Temp.</u>	<u>Aux. Temp.</u>	<u>L</u>	<u>Therm. Corr.</u>	<u>Corr. Temp.</u>
10.00	144.9	52	60	-0.1	145.7
18.00	126.2	49	41	0	126.7
19.00	123.9	48	39	0	124.4
20.00	122.1	48	37	0	122.8
20.70	121.4	47	36	0	121.8
21.50	122.5	51	37	0	122.9
28.00	144.5	50	60	-0.1	145.3

Table 6 - Micro Method on Recrystallized NaNO_3

12.46	139.3	60	49	0	139.9
18.77	124.7	53	36	0	125.1
21.46	121.8	55	33	0	122.1
27.90	144.8	62	55	-0.1	145.4

Table 7 - Macro Method on Precipitated NaNO_3

10.00	144.8	45	60	-0.1	145.6
19.00	124.2	57	39	0	124.6
20.00	122.6	54	38	0	123.0
21.50	122.2	45	37	0	122.6
28.00	144.6	47	60	-0.1	145.4

Table 8 - Micro Method on Precipitated NaNO_3

10.47	144.3	55	56	-0.1	145.0
18.94	124.2	43	35	0	124.6
21.84	122.5	55	34	0	122.9
28.05	145.0	58	55	-0.1	145.6

DISCUSSION OF RESULTS

Figure 6 shows the very close agreement obtained even when materials are purified by different methods. This and Figure 5 also show that consistent results can be secured, using either the macro or the micro methods. A comparison of Figures 5 and 6 results in the conclusion that the mode of drying only very, very slightly affects the results. In fact, any slight experimental error will cause a much greater affect than will the mode of drying.

Finally, from the data presented, it can be concluded that the phase diagram for the system, ammonium nitrate-sodium nitrate, as presented by Early and Lowry,^(1,2) is unreliable. Table 9 can be said to be the representative value of this work for that particular system, and is shown graphically in Figure 7.

Table 9 - Average Results

<u>% NaNO₃</u>	<u>Temperature</u>
0	169.6
10.0	145.7
18.0	126.7
19.0	124.4
19.6	123.3
20.7	121.8
22.5	126.6
28.0	145.3

FIG. 6

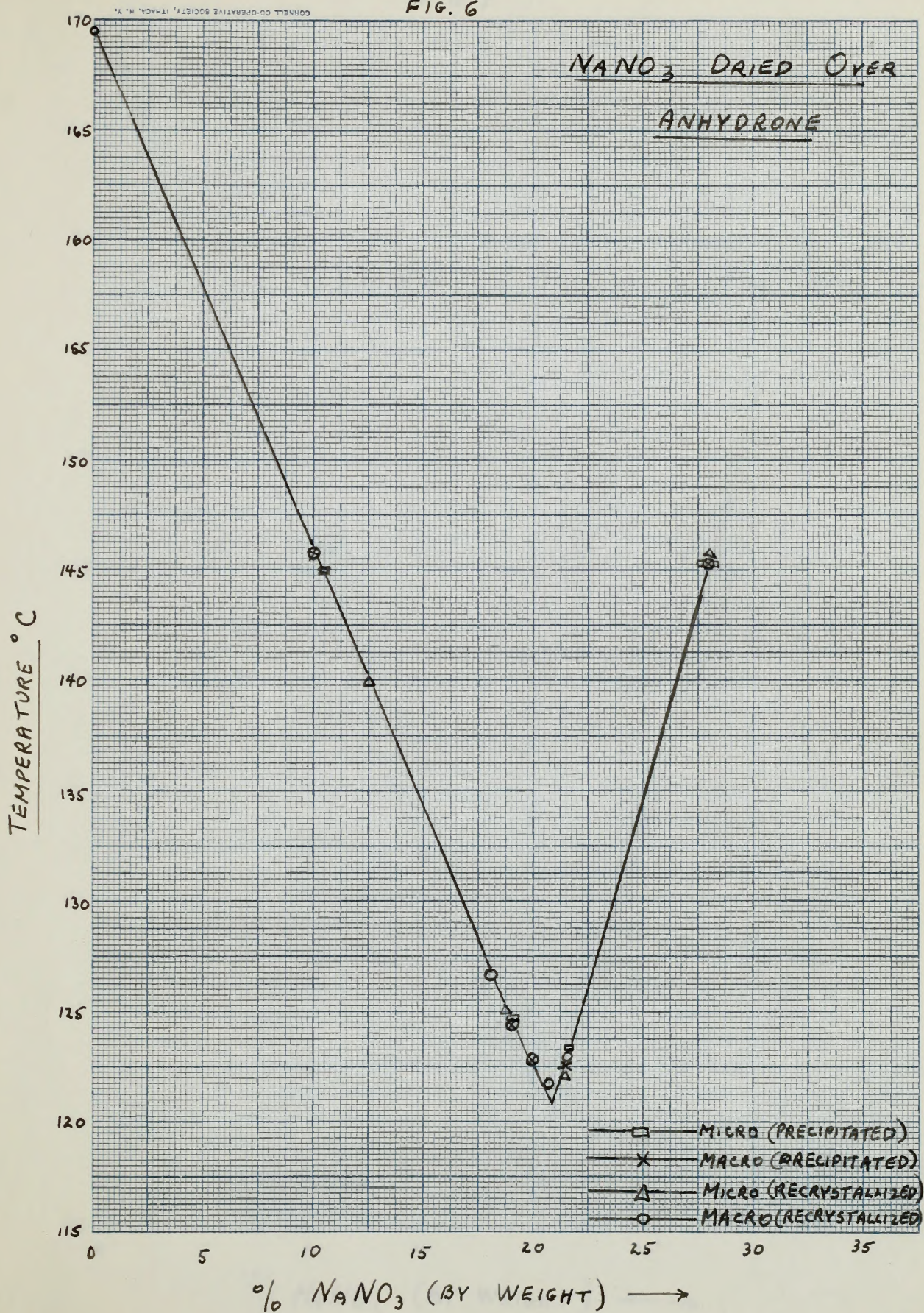
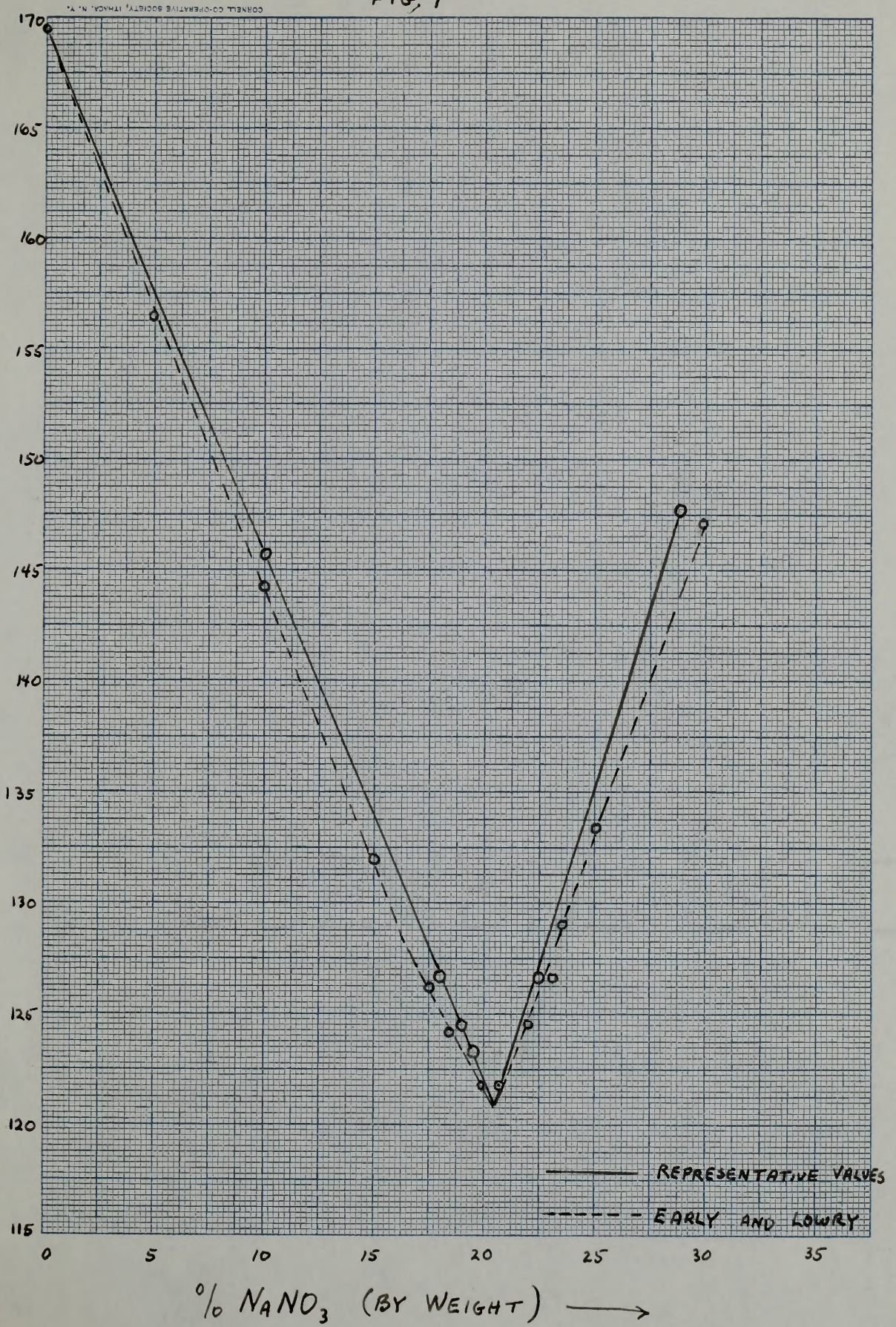


FIG. 7



SUMMARY

The micro and the macro methods have been used in the determination of the phase diagram of the system, ammonium nitrate - sodium nitrate. From the results of the experimental work, the following facts can be concluded.

(1) As long as the components used are pure, it makes no difference in the results which way this purity is obtained.

(2) The type of solid dryer used, whether it be anhydrous calcium chloride or Anhydrone, does not affect the results. Of course, a sufficient length of time must be allowed for the calcium chloride to exert its influence.

(3) The data of Early and Lowry,^(1,2) which is acknowledged as standard by the National Research Council, is unreliable.

(4) Either the use of the macro or the micro method for the determination of phase diagrams is satisfactory, since consistent checks may be obtained.

The data which is brought forward to replace the standard values is as follows:

<u>% NaNO₃</u>	<u>Temperature</u>
0	169.6
10.0	145.7
18.0	126.7
19.0	124.4
19.6	123.3
20.7	121.8
22.5	126.6
28.0	145.3

The eutectic temperature found was 121.0°C. while the corresponding percentage composition was 20.5%. These points were the only ones that checked the work of Early and Lowry.^(1,2)

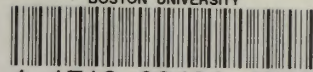
FOOTNOTES

- (1) Early, R.G., and Lowry, T.M., "J. Lond. Chem. Soc.," 115,
1387, (1919)
- (2) Early, R.G., and Lowry, T.M., "J. Lond. Chem. Soc.," 121,
963, (1922)
- (3) Holmes, E.O., Jr., and Mason, J.P., Private Communication.

NOTES

- (1) Survey of the ...
(1917-1918)
- (2) Survey of the ...
(1919-1920)
- (3) Survey of the ...
(1921-1922)

BOSTON UNIVERSITY



1 1719 02481 4370

ACCOPRESS BINDER
NO. BF 250 P7 Embossed

Made by ACCO PRODUCTS, INC.
Long Island City, N. Y., U. S. A.

